DEC 17 1996

SANDIA REPORT

SAND96–2712 • UC–704
Unlimited Release
Printed November 1996

The Effect of Silica-Containing Binders on the Titanium/Face Coat Reaction

DEC 20 1996
OSTI

C. Frueh, D. R. Poirier, M. C. Maguire

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SF2900Q(8-81)

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
US Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

SAND96-2712
Unlimited Release
Printed November 1996

Distribution
Category UC-704

The Effect of Silica-Containing Binders on the Titanium/Face Coat Reaction

C. Frueh and D. R. Poirier
Department of Materials Science and Engineering
University of Arizona, Tucson, AZ 85721

M. C. Maguire
Liquid Metal Processing Laboratory
Sandia National Laboratories, Albuquerque, NM 87185-1134

Abstract

The interactions of CP-Ti and Ti-6Al-4V with investment molds containing alumina/silica and yttria/silica face coat systems were studied. Containerless melting in a vacuum was employed and small test samples were made by drop casting into the molds. The effects of the face coat material and mold preheat temperatures on the thickness of the alpha case on the castings were evaluated with microhardness and microprobe measurements. It was found that the thickness of the alpha case was the same, whether a yttria/silica or alumina/silica face coat was used, indicating that the silica binder reacted with the titanium. Hence, the use of expensive refractories, such as yttria, represents an unnecessary cost when combined with a silica binder. It was also found that the alloyed titanium castings had a thinner alpha case than those produced from CP-Ti, which suggests that the thickness of the alpha case depends on the crystal structure of the alloy during cooling from high temperatures. Furthermore, castings made in small yttria crucibles used as molds exhibited little or no alpha case.

Acknowledgment

The authors appreciate the support of an Associated Western Universities - Department of Energy Fellowship. Techical insight and discussions with A. Yasrebi of Precision Castparts Corp., Portland, OR, D. Mustoe of Custom Technical Ceramics, Arvada, CO, and L. Gonnsen of Sandia National Laboratories, Albuquerque, NM, are greatly appreciated.

Contents

Figures

Introduction

Three factors have made the production of quality titanium castings a difficult task: (1) titanium has a high melting point; (2) it has low fluidity at pouring temperatures; and (3) it is highly reactive with nearly all gasses, liquids, or solids when at temperatures above 500°C[1]. Although each factor presents processing difficulties, it is the third which most hinders the capability of titanium casting technology. Liquid titanium has been termed "the universal solvent"[2] because violent reactions with gasses, liquids, and solids results in contamination of the titanium. Furthermore, titanium has a high affinity for interstitials such as nitrogen, oxygen, and carbon, and only small concentrations of these interstitials are enough to deleteriously affect its ductility[3,4].

During solidification, a reaction occurs between a titanium casting and its shell mold. The result of this interaction is an oxygen-enriched surface layer, known as the alpha case. If a casting is to be used in a critical application, then this layer must be removed, usually by chemical milling. Because this removal process is waste producing, expensive, and limits the complexity and detail that can be achieved in a casting, much effort, has gone into trying to develop a mold material that does not react with titanium. To date, however, no such shell mold has been developed for producing titanium investment castings that are free of the alpha case.

A review of past papers, patents, and reports is given elsewhere[5]. The review also gleans information that resulted from efforts to develop a refractory crucible for containing liquid titanium. This information can be of benefit provided one is not too hasty to eliminate a material from consideration as a mold material because it was shown not to function well as a crucible. For example, Chapin and Friske[6-8], investigated the use of various oxides, carbides, borides, a sulfide, carbon and graphite as possible container materials for titanium. They found that none of the selected materials were inert to titanium. Titanium melted in a thoria crucible was found to contain an average of 5.44% thoria; if thoria had been tested as a mold material, however, it is possible that very little or no contamination would have been detected.

Thermodynamics can also help the investigator identify materials which should be tried. An analysis typically involves a comparison of the free energy of formation of the candidate refractory to that of the corresponding titanium phase. This is a rather simplistic approach because, as indicated by Saha et al.[9], it neglects solution effects. In addition most commercial binders in ceramic shell molds are made from colloidal silica[10], so regardless of the chemical stability of a refractory, its effectiveness will be undermined by the presence of the siliceous binder. In this context, Saha et al.[9] evaluated rare earth oxides for use in face coats for investment casting titanium and found yttria to fare the best.

Assuming an acceptable yttria slurry could be developed and its use results in reducing the thickness of the alpha case, one should ask whether it is economic. According to Prigent and Debuigne[11], the use of yttria would be limited by its "prohibitive cost." Indeed, the \$40-\$80/lb[12], price tag for yttria seems very high, especially when compared to the cost of materials such as alumina, silica, and even zirconia. This paper does not, however, question the expense of materials such as yttria but whether the expense is really necessary. One objective of this work is to determine whether the presence of a siliceous binder drives the Ti/mold reaction, regardless of the refractory used.

Experimental Procedure

A. Mold Production

A face coat slurry and a backup coat slurry were used to make the shell molds. Both slurries used a commercially available binder in conjunction with a refractory. The binders used for the face coat and backup coat were Primcote™(Ransom & Randolph, Maumee, OH 43537) and Nyacol

830 (PQ Corp., Valley Forge, PA 19482), respectively. For the shell system with the alumina/silica face coat the Primcote was combined with Remasil-60 (aluminosilicate) and RP-1 (fused silica), both from Remet Corporation (Chadwicks, NY 13319). The powders (-325 mesh) were added in a 10:1 ratio, respectively. The viscosity of the slurry was kept between 20-30 s, measured in Zahn cup 5; deionized water was added as necessary to adjust the viscosity. The shell system with the yttria/silica face coat used a slurry made in the same manner except yttria powder was used instead of the Remasil-60 and RP-1. Although this work did not require slurries with a long "shelf-life," it is of interest to note that the yttria slurry gelled much sooner than its counterpart, as was also observed by Calvert[13]. The backup slurry for both molds used Nyacol 830 binder in combination with RP-2 (fused silica) from Remet Corporation.

The molds were built up, around a cone-shaped wax pattern with an opening diameter of 25 mm and a height of 19 mm. Build-up was achieved by dipping the pattern in the appropriate slurry, sprinkling with a stucco, and allowing it to dry in a controlled humidity chamber, as typical in an investment casting process. The face coat slurry was used to produce the first two layers, and the backup coat slurry was used for the four succeeding layers and as the seal coat. The composition and particle size distribution of each of the six stucco coats were the same for both types of molds.

B. Melting Furnace

Figure 1 shows the furnace used to produce the titanium castings. Two induction power supplies were used: a 30 kW, 450-500 kHz, generator was used for melting, and a 2 kW, 550 kHz, generator was used for mold-preheating through the use of a graphite susceptor. The charge for the melt was hung with titanium wire, and the susceptor/mold fixture was supported with alumina tubing.

As can be seen in Figure 1, melting and casting took place inside a quartz tube. The environment inside the tube was provided by a vacuum system and a gas source. The benefits of using this system was that it was "containerless" and melting and casting were done in an inert atmosphere.

C. Casting Experiments

Slugs of CP-Ti (ASTM B-348, Grade 1) and Ti-6Al-4V(AMS-4928M, Grade 5), that weighed 4 g each, were suspended at a fixed distance from the top of the mold with CP-Ti wire. The chamber was evacuated with a mechanical pump to 10^{-1} torr, backfilled with ultra-high purity argon and evacuated again. With the mechanical pump still on, the mold was slowly heated to 400°C and allowed to outgas for 30 minutes. Mold temperature was measured by focusing an optical pyrometer on the face coat. Then the mold was either heated or allowed to cool to a preheat temperature; preheat temperatures of 25, 350, 500, 650, and 800°C were selected. When the desired preheat temperature was reached, the valve to the mechanical pump was closed and the valve to a turbomolecular pump was opened. After the vacuum stabilized, the chamber was backfilled with argon, and evacuated again. This procedure was continued until a vacuum of < 2 x 10-5 torr was reached. Prior to melting, the chamber was backfilled to 1/3 psig with argon, the mold preheat coil was deenergized, and the melt coil energized. The chamber was kept at 1/3 psig with argon during and after the melt.

Because of the position of the slug prior to melting, and the configuration of the coil, the titanium melted from the bottom up. The electromagnetic field and surface tension force held the droplet until the melt pool reached the wire, when the droplet fell into the mold. Melting took approximately 20 s and the casting was kept in the argon until cool. Figure 2 shows a cross section of a casting in its mold.

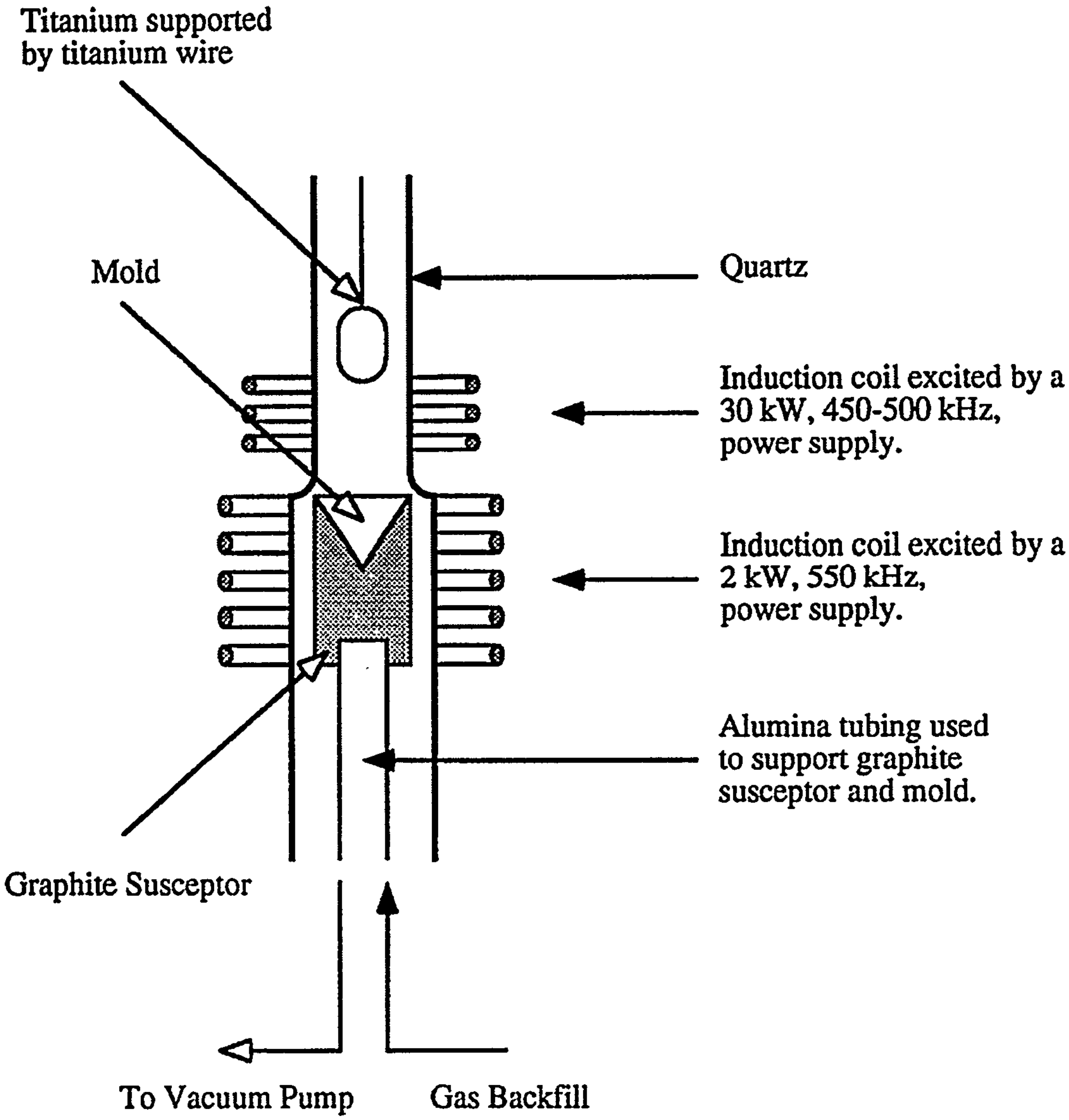


Figure 1. The containerless melting apparatus used to produce castings.

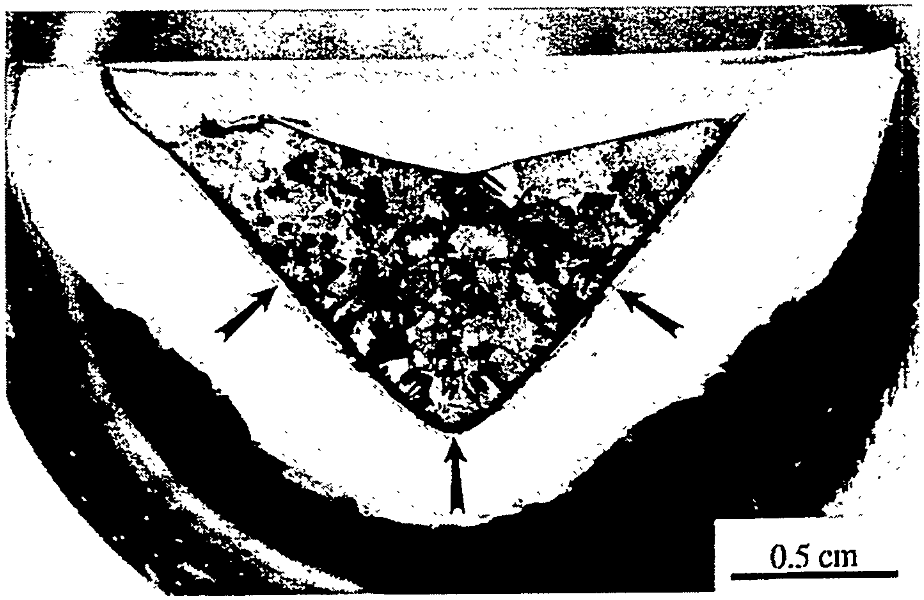
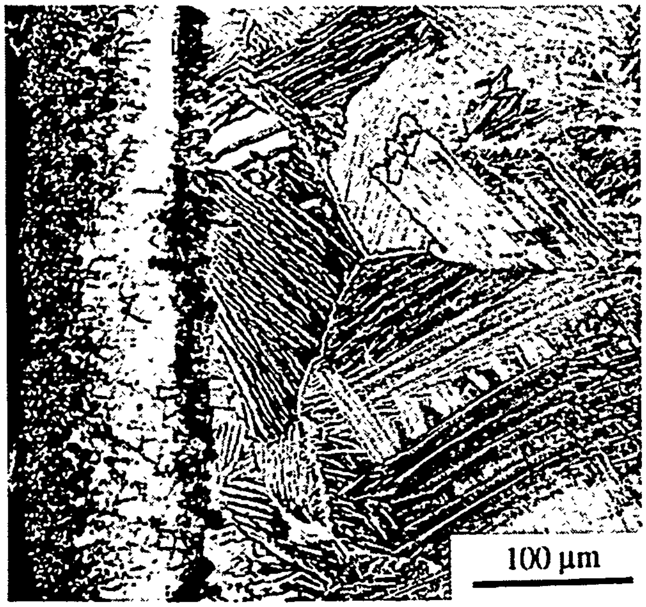


Figure 2. Cross section of a casting and its mold; the arrows point to microhardness traverses.

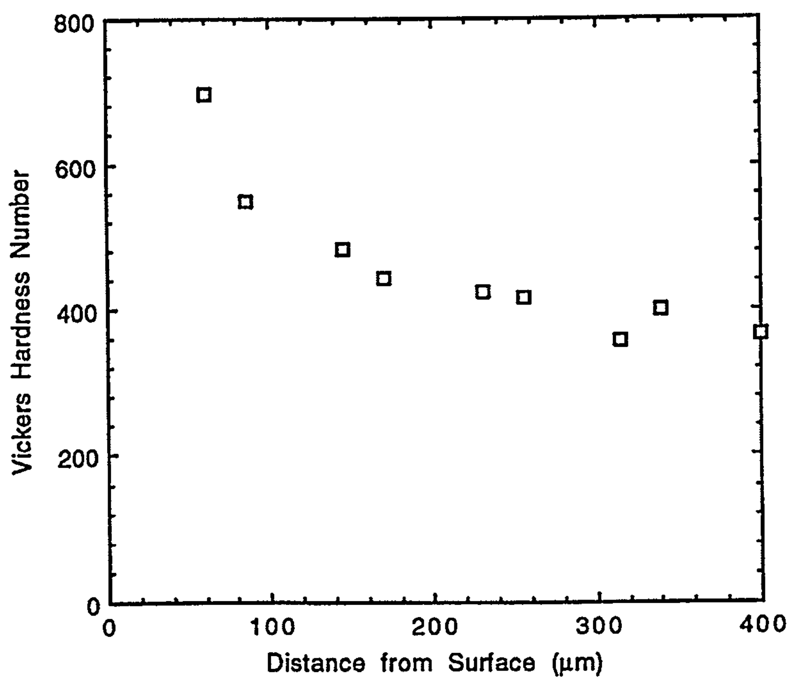
D. Analysis of Castings

Saha et al.[14], confirmed that microhardness profiles can be used to determine the thickness of the alpha case to indicate the diffusion profile of oxygen at the surface of the casting. In our work, three Vickers-microhardness traverses were made, using a 100 g load held for 15 s on a Shimadzu hardness tester. The arrows in Figure 2 indicate the locations and directions of the three traverses. Each indentation was made at a specific distance from the surface; for example, if the first indentation in one traverse was 150 μm away from the surface, then the first indentations in the other two traverses were also at 150 μm from the surface. This procedure provided for an average Vickers hardness number (VHN) based on three measurements at a specific distance from the surface.

Figure 3 shows a microstructure and a hardness profile in Ti-6Al-4V that was cast in a mold with an alumina/silica face coat preheated to 500°C. The thickness of the alpha case is taken as the distance where the hardness value returns to a nominal value. In this example, the nominal value is approximately 380 VHN, which in turn corresponds to an alpha case with a thickness of 360 μm. The surfaces of the CP-Ti castings were also evaluated using a microprobe. Area elemental distribution (EDPMs) and secondary electron (SEM) and backscattered electron (BES) micrographs were taken with an accelerating voltage of 15 keV. In addition, quantitative analyses were made using software based on the usual corrections for matrix effects. The elements of interest were calibrated with elemental standards, and the analyses were done in 1 μm steps.



(a)



(b)

Figure 3. Microstructure and hardness profile from a Ti-6Al-4V casting made in a mold with an alumina/silica face coat preheated to 500°C. (a) Microstructure etched with Kroll's reagent and (b) corresponding microhardness plot.

Results and Discussion

A. Microhardness Results

Figure 4 shows microhardness profiles of the CP-Ti castings made in molds with an alumina/silica face coat. Castings were produced in molds at room temperature (RT), and in molds preheated to 350, 500, 650 and 800°C, but only profiles at RT and 800°C are plotted in order not to overload the plots with data. In Figure 4 it can be observed that as the mold preheat temperature rises the hardness increases, an indication of more contamination resulting from preheating. Note, however, that the preheat temperature does not greatly influence the apparent thickness of the alpha case.

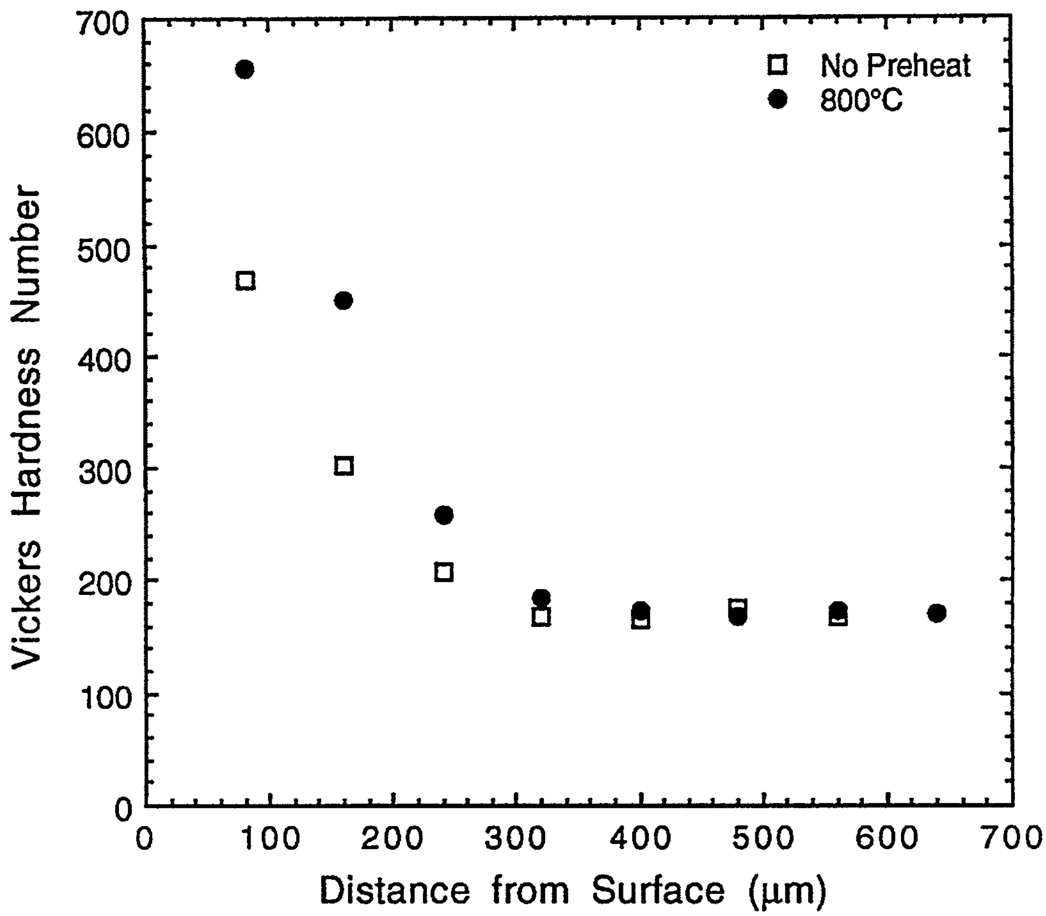


Figure 4. Microhardness profiles of CP-Ti castings produced in molds having an alumina/silica face coat.

The microhardness profiles in the Ti-6Al-4V castings were similar to those in Figure 4, although it did appear that the reaction layer was slightly thinner. Figure 5 illustrates this by comparing castings made in molds preheated to 350°C. An explanation for the difference could be the allotropic nature of titanium. Upon cooling, CP-Ti undergoes a transformation from a body-centered cubic structure (the beta phase) to its hexagonal close-packed phase (the alpha phase) at

882°C. The addition of aluminum to titanium raises the beta transus to 980°C[15]. Because interstitials, in this case oxygen, are able to diffuse more readily in a body-centered cubic lattice[16], more oxygen is able to diffuse into the CP-Ti because it retains its beta-structure longer.

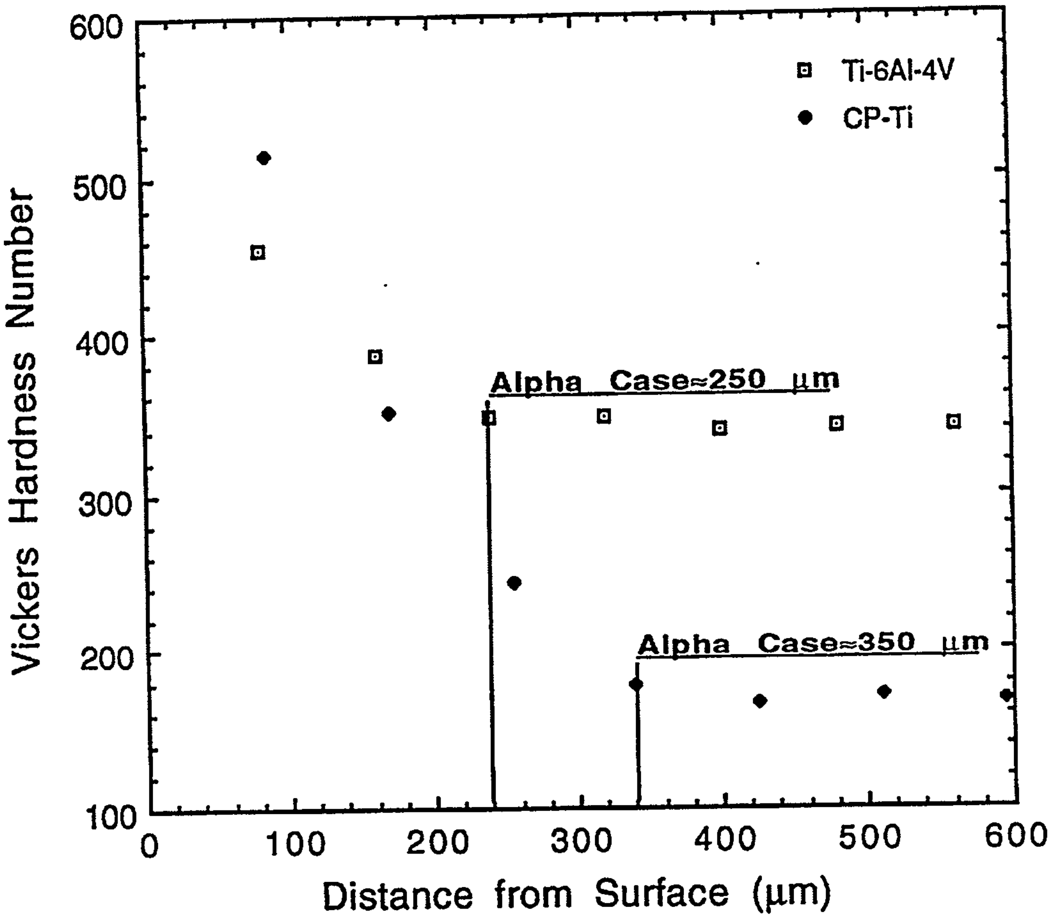


Figure 5. Microhardness profiles of castings (CP-Ti and Ti-6Al-4V) produced in molds, preheated to 350°C, having an alumina/silica face coat.

Figure 6 shows the effect of mold preheat temperature on the reaction between CP-Ti and the yttria/silica face coat. The results are similar to those seen in Figures 4 and 5, in that the higher mold preheat temperature resulted in higher hardnesses in the alpha-case layer. Once again, the results obtained from the alloyed titanium were similar to those from the CP-Ti, with the exception that the thickness of the alpha case was greater on the CP-Ti castings than on the Ti-6Al-4V castings.

It is of interest to note that the castings produced in molds with an alumina/silica face coat stripped cleanly from their molds, whereas those produced in the molds with a yttria/silica face coat adhered to the molds and caused the face coat to spall off upon separation from the casting. Figure 7 shows a secondary electron micrograph of the surface of a CP-Ti casting made in a preheated mold (800°C) with a yttria/silica face coat. From the figure it can be determined that titanium has penetrated the face coat, possibly because the yttrium oxide-refractory did not sinter enough. Calvert[13], found that firing temperatures of at least 1200°C were required; in fact, the best results came from a mold which was fired in a vacuum furnace at 1500°C.

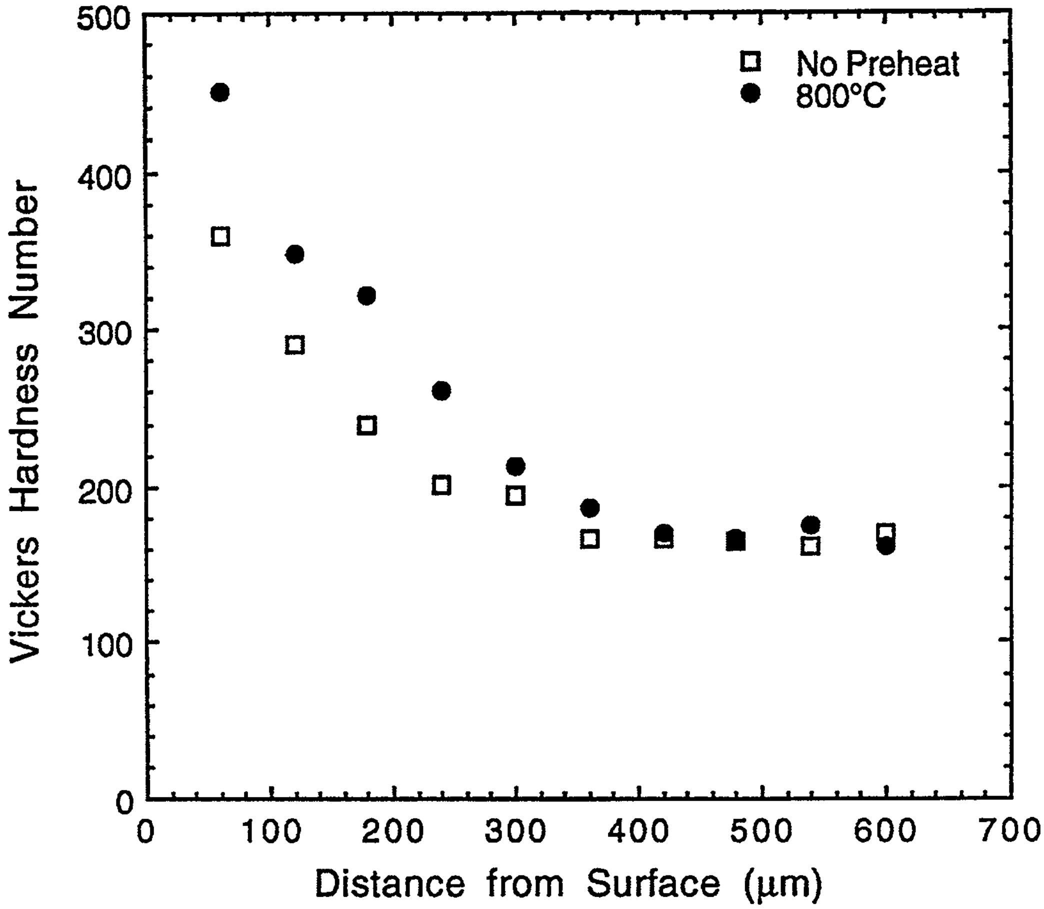


Figure 6. Microhardness profiles of CP-Ti castings produced in molds having a yttria/silica face coat.

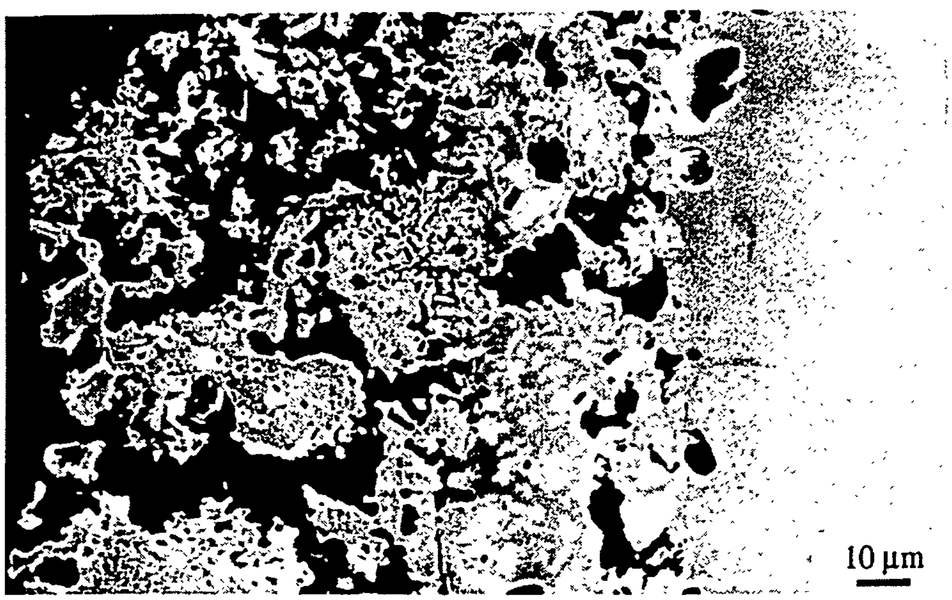


Figure 7. Microstructure (SEM image) of a CP-Ti casting made in a mold with a yttria silica face coat, preheated to 800°C.

The thickness of the metal-penetration shown in Figure 7 varied between 30 and 50 μm, depending on the mold preheat temperature. Castings produced in molds at room temperature had layers which were approximately 30 μm in thickness; castings produced in molds at 800°C had layers closer to 50 μm in thickness. All other castings had layers that were between 30 and 50 μm in thickness.

By comparing data of the titanium-yttria/silica face coat interaction to data of the titanium-alumina/silica face coat interaction, it becomes apparent that no benefit is gained through the incorporation of the more thermodynamically stable yttria within the face coat. Even though the plots show that the yttria/silica face coat resulted in somewhat lower hardnesses in the alpha case, the thickness of the alpha case, and the hardnesses beyond the alpha case are the same as those resulting from casting against an alumina/silica face coat.

B. Microprobe Results

In order to explain why the incorporation of a more stable refractory in the facecoat did not reduce the thickness of the alpha case, microprobe analyses were carried out. From Figure 8, it is apparent that the reaction between a titanium casting and a yttria-rich face coat is fueled by the oxygen resulting from the decomposition of silica, not yttria. Figure 8 shows that only silicon has diffused into the casting, indicating that the yttria was left intact.

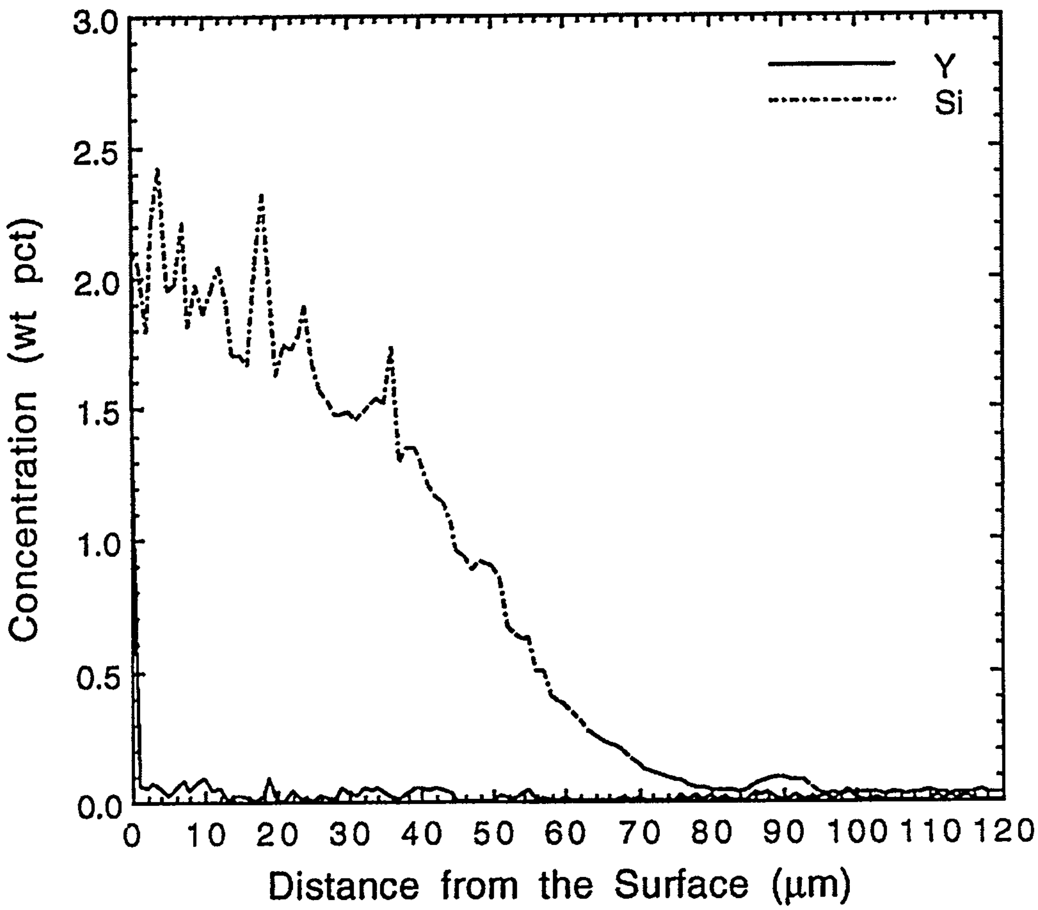


Figure 8. Concentration of yttrium and silicon which has diffused into a CP-Ti casting as a result of its contact with a yttria/silica face coat with no preheat.

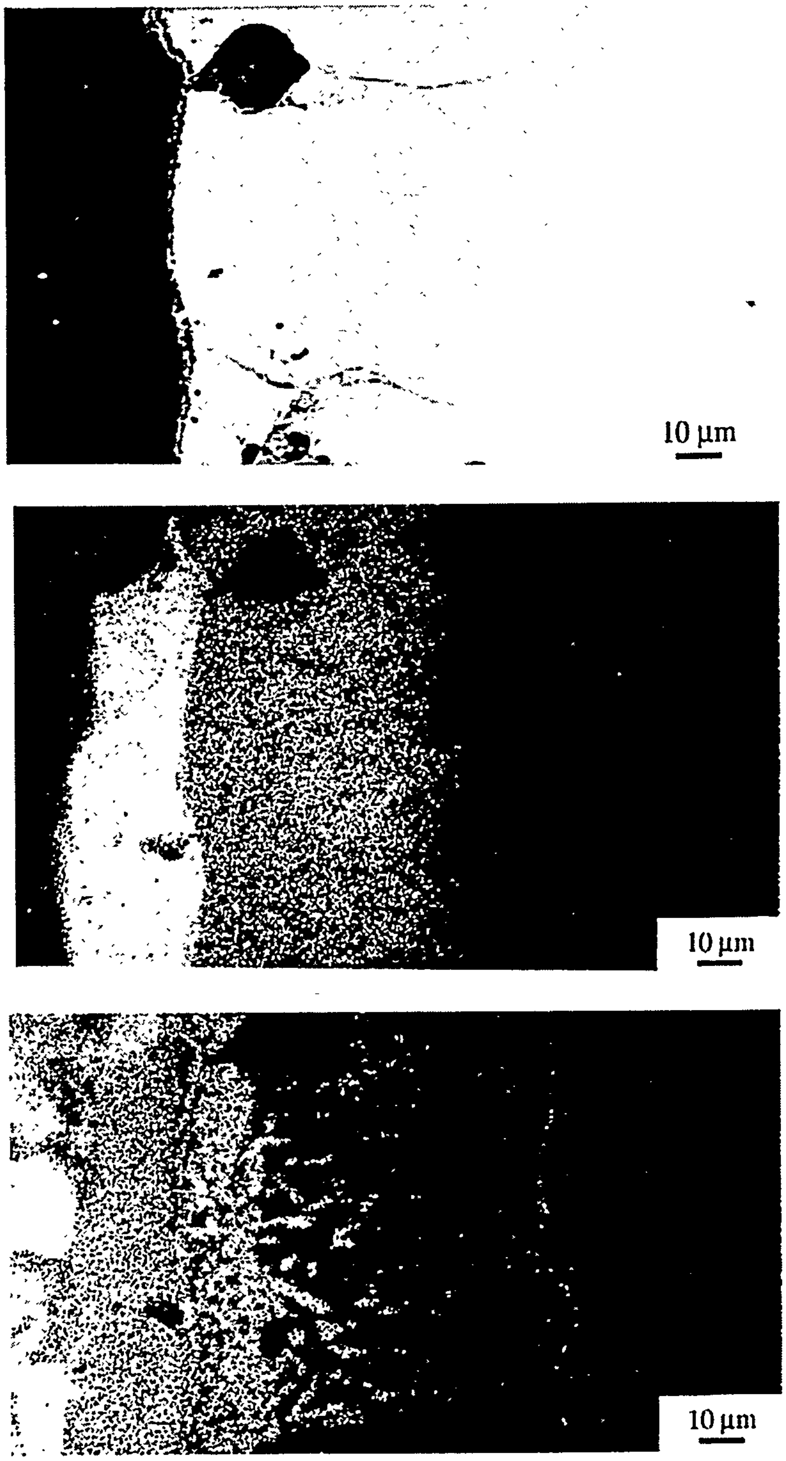
In castings made in molds with alumina/silica face coats, aluminum was also found with silicon dissolved in the alpha case layer. This is observable in Figure 9(b), which shows a significant amount of aluminum in a CP-Ti casting made in a mold with an alumina/silica face coat preheated to 800°C. Figure 9(a), a backscattered electron micrograph of the mapped region, is provided to ensure that the metal/mold interface is recognizable. The cracks should also be noted, as they indicate the brittle nature of the alpha case. Figure 9(c) is included to illustrate that the silicon diffused into the casting in a different manner than the aluminum. While the aluminum is evenly dispersed, the distribution of Si has fingers ahead of the overall diffusion layer. This suggests the formation of a low-melting eutectic or grain boundary diffusion. Saha and Misra[17] indicated the formation of the low-melting Ti_5Si_3+Ti eutectic at the metal-mold interface during the casting of Ti in zircon ($ZrSiO_4$) sand molds. Although it was not determined whether this phase was a result of the interaction of titanium with free silica or silica derived from the zircon sand, the results did indicate that if the amount of silica was lessened, then the Ti/mold reaction was likewise lessened.

C. Analysis of Castings Produced in 100% Yttria Molds

Based on the above results, it appears that the concentration of oxygen at the Ti/mold interface is set by the partial pressure of oxygen resulting from the reduction of silica. Therefore, in order to realize the benefit of using yttria one must eliminate the silica. To determine whether this was indeed the case, an effort was made to make a face-coat slurry from yttria particles and yttrium acetate as the binder. Yttrium acetate converts to the oxide at elevated temperatures. Three problems were encountered: rapid and instantaneous: gelation of the slurry, lack of green strength, and lack of mold strength after firing. We were not able to overcome these problems, so yttria crucibles (22 mm in diameter, 27 mm tall, and 2 mm wall thickness) were purchased and used as molds.

Figure 10 shows microhardness plots of CP-Ti and Ti-6Al-4V castings produced in crucibles preheated to 800°C. As indicated by the plots, yttria appears to be an excellent mold material for titanium as there is no indication of an alpha case. Figure 11, which shows an optical micrograph of the surface of a Ti-6Al-4V casting solidified in a yttria mold, further supports this observation, especially when it is compared to Figure 3(a).

By comparing microhardness data from castings produced in yttria crucibles with data from castings produced in molds with yttria/silica face coats (Figure 12), it becomes apparent that the benefits of yttria are not realized when it is combined with a silica binder. Furthermore, these data indicate that if a silica-free yttria face coat were developed, then the alpha case would be reduced significantly or perhaps even eliminated. It must be remembered, however, that the castings produced in this study were quite small and cooled quickly. Feagin[18,19] however, reported encouraging results when he cast Ti-6Al-4V in molds, with a near 100% yttria face coat, which were larger (10 cm) and found an alpha case of less than 3 μm.



(a)

(b)

(c)

Figure 9. The alpha case of a CP-Ti casting made in a mold with an alumina/silica face coat reheated to 800°C. (a) Backscattered electron micrograph; (b) 20 wt pct aluminum map; and (c) 20 wt pct silicon map. The large silicon-rich particles in (c), located to the left side, are glass particles in the epoxy mounting material.

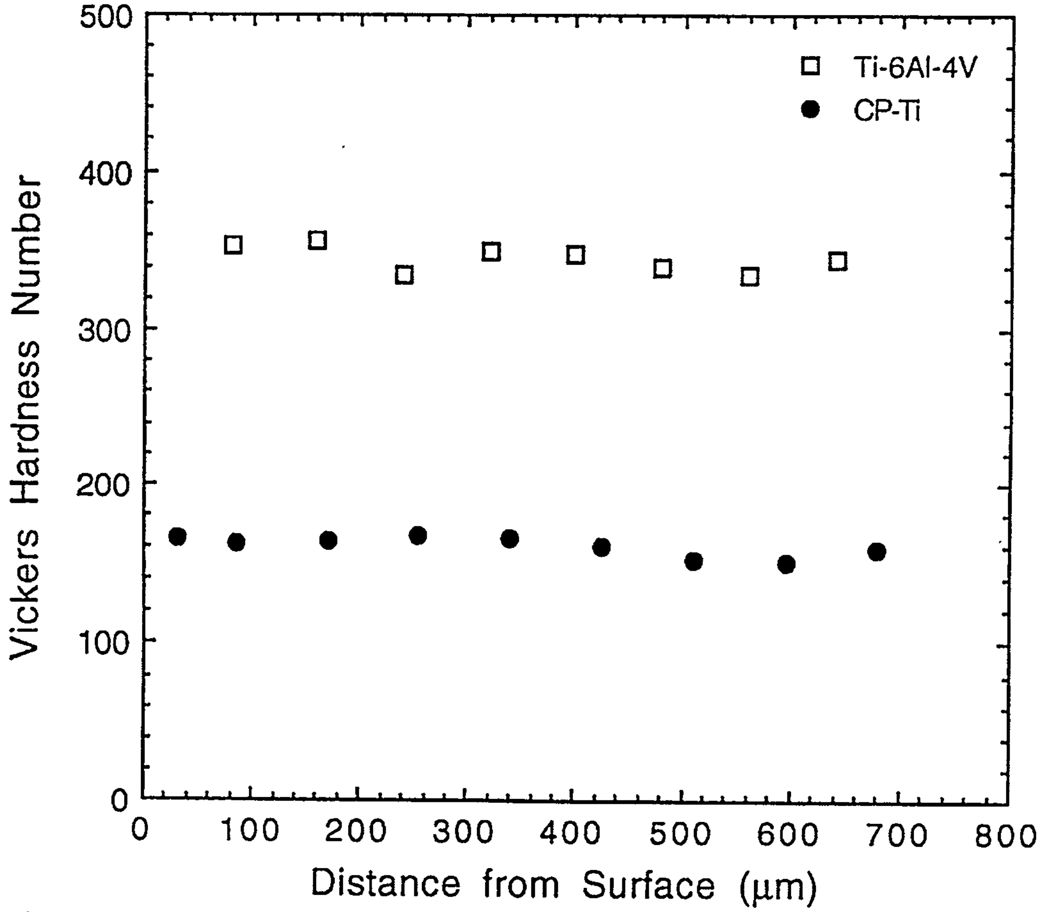


Figure 10. Microhardness profiles of CP-Ti and Ti-6Al-4V castings produced in yttria molds preheated to 800°C.

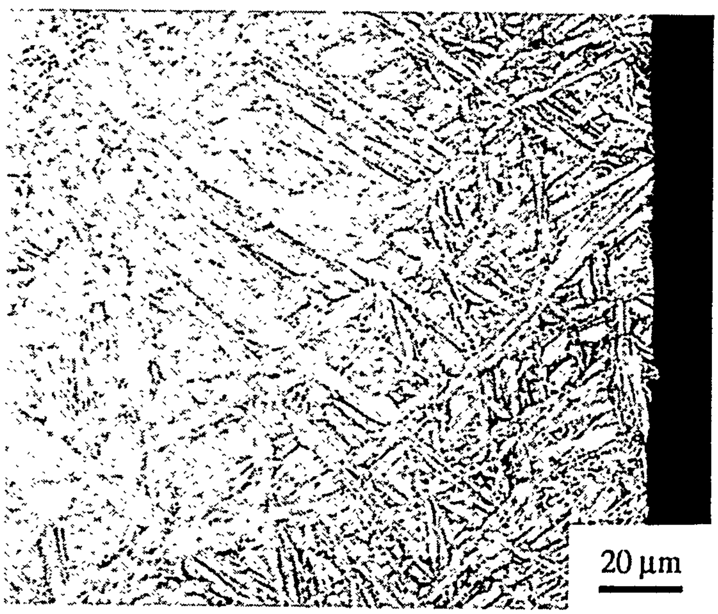


Figure 11. Micrograph of Ti-6Al-4V casting produced in a yttria mold preheated to 800°C. Etched with Kroll's reagent.

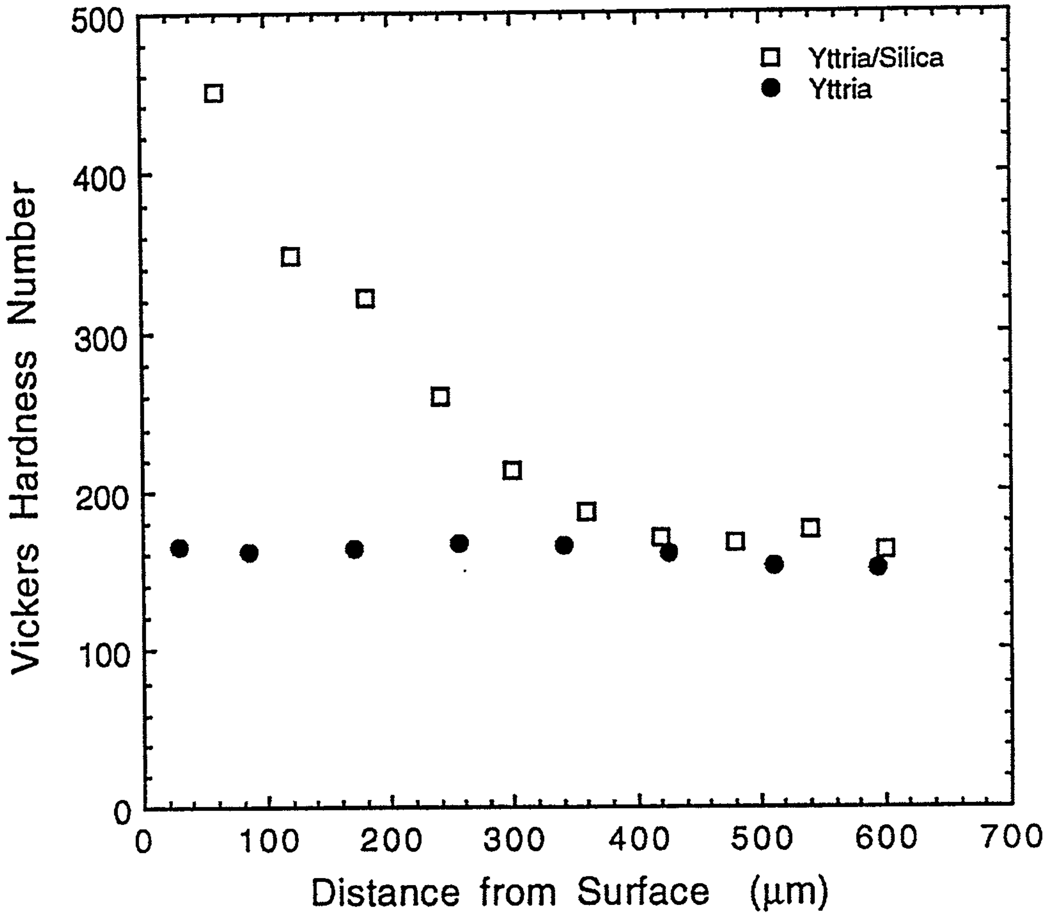


Figure 12. Microhardness profiles from CP-Ti castings produced in either a yttria crucible or a mold having a yttria/silica face coat; molds were preheated to 800°C.

Conclusions

In this research, the effect of face coat composition on the reaction between titanium and an investment shell mold was investigated in order to identify the culprit responsible for the production of alpha case on titanium castings. The major conclusions of this research are the following:

(1) Silica, used as a binder for investment shell mold, drives the Ti/mold reaction regardless of the refractory used.

(2) The use of a thermodynamically stable refractory, such as yttria, in a face coat represents an unnecessary expense when combined with a silica binder.

(3) Using yttria as a face coat material could be an excellent way to reduce the alpha case, if a silica free binder is developed.

(4) Ti-6Al-4V castings had a thinner alpha case than those produced from CP-Ti.

References

1. P. J. Bridges and F. Hauzeur: *Cast Metals,* 1991, vol. 4, pp. 152-54.

2. A. Mitchell and D. W. Tripp: *SAMPE Quart.,* 1989, vol. 20, pp. 38-41.

3. R. I. Jaffee and I. E. Campbell: J. *of Met.,* 1949, vol. 185, pp. 646-54.

4. W. L. Finlay and J. A. Snyder: J. *of Met.,* 1950, vol. 188, pp. 277-86.

5. C. Frueh, M. C. Maguire, and D. R. Poirier: J. *Am. Cer. Soc.,* 1995 (submitted).

6. E. J. Chapin and W. H. Friske: Naval Research Laboratory, Washington, DC, NRL Report 4447, 1954.

7. E. J. Chapin and W. H. Friske: Naval Research Laboratory, Washington, DC, NRL Report 4467, 1954.

8. E. J. Chapin and W. H. Friske: Naval Research Laboratory, Washington, DC, NRL Report 4478, 1955.

9. R. L. Saha, T. K. Nandy, R. D. K. Misra, and K. T. Jacob: *Metall. Trans.* B, 1990, vol. 21B, pp. 559-66.

10. M. J. Hendricks and G. R. Maxwell: "Process Influences on Effective Slurry Life, presented at the *40th Annual Meeting of the Investment Casting Institute* (Las Vegas, NV), 1992, pp. 10: 1-10:9.

11. S. Prigent and J. Debuigne: "A New Calcia Technology for Investment Casting of Titanium Alloys with the Lost Wax Process," in *Titanium '92 Science and Technology,* F. H. Froes and I. Caplan (eds.), The Minerals, Metals, and Materials Society, Warrendale, PA, 1993, pp. 1519-26.

12. Dave Mustoe: Custom Technical Ceramics, Arvada, CO, private communication, 1994.

13. E. D. Calvert: Bureau of Mines Report of Investigations, RI 8541, 1981.

14. R. L. Saha,T. K. Nandy, R. D. K. Misra, and K. T. Jacob: *Bull. Mat. Sci. (India),* 1989, vol. 12, pp. 481-93.

15. M. J. Donachie, Jr. (ed.): *Titanium: A Techn.ical Guide,* ASM International, Metals Park, OH, 1988, p. 106.

16. P. G. Shewmon: *Diffusion in Solids,* J. Williams Book Co., Jenks, OK, 1983,pp.134-5.

17. R. L. Saha and R. D. K. Misra: J. *Mat. Sci. Letters,* 1991, vol. 10, pp. 1318- 19.

18. R. C. Feagin: European Patent 0204674, Remet Corp., Chadwicks, NY, 1986.

19. R. C. Feagin: "Casting of Reactive Metals into Ceramic Molds," in*Proceedings of the Sixth World Conference on Investment Casting,*Washington, DC, 1984, pp. 4:01-4:13.

DISTRIBUTION:

1	MS9018	Central Technical Files, 8523-2
5	MS0899	Technical Library, 4414
2	MS0619	Review and Approval Desk, 12630 For DOE/OSTI
1	MS0513	R.J.Eagan, 1000
1	MS1435	H.J. Saxton, 1800
1	MS1134	W.R. Hammetter, 1846
5	MS1134	M.C. Maguire, 1846
1	MS1134	F.J. Zanner, 1846

5 University of Arizona
Department of Materials Science and Engineering
Attn: Prof. D.R. Poirier
Tucson, AZ 85721

5 University of Arizona
Department of Materials Science and Engineering
Attn: C.A. Frueh
Tucson, AZ 85721